

Project Title: **“Laboratory Experiments and Instrument Intercomparison Studies of Carbonaceous Aerosol Particles”**

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**FINAL PROGRESS REPORT**

**Objectives of the Project**

Aerosols containing black carbon (and some specific types of organic particulate matter) directly absorb incoming light, heating the atmosphere. In addition, all aerosol particles backscatter solar light, leading to a net-cooling effect. Indirect effects involve hydrophilic aerosols, which serve as cloud condensation nuclei (CCN) that affect cloud cover and cloud stability, impacting both atmospheric radiation balance and precipitation patterns. At night, all clouds produce local warming, but overall clouds exert a net-cooling effect on the Earth. The effect of aerosol radiative forcing on climate may be as large as that of the greenhouse gases, but predominantly opposite in sign and much more uncertain. The uncertainties in the representation of aerosol interactions in climate models make it problematic to use model projections to guide energy policy.

The objective of our program is to reduce the uncertainties in the aerosol radiative forcing in the two areas highlighted in the ASR Science and Program Plan. That is, (1) addressing the direct effect by correlating particle chemistry and morphology with particle optical properties (i.e. absorption, scattering, extinction), and (2) addressing the indirect effect by correlating particle hygroscopicity and CCN activity with particle size, chemistry, and morphology. In this connection we are systematically studying particle formation, oxidation, and the effects of particle coating. The work is specifically focused on carbonaceous particles where the uncertainties in the climate relevant properties are the highest. The ongoing work consists of laboratory experiments and related instrument inter-comparison studies both coordinated with field and modeling studies, with the aim of providing reliable data to represent aerosol processes in climate models.

During the past three years and the fourth year of a no-cost extension our work has proceeded along the lines described in our original proposal. We report on 12 completed and/or continuing projects conducted during the period 08/14/2011 to 08/14/2015. These projects are described in 17 manuscripts that have been published in refereed journals. Several manuscripts are in preparation.

A glossary of abbreviations is listed at the end of this report.

**1. Aerosol Mass Spectrometry of Black Carbon (BC)-Containing Particles With the SP-AMS Instrument.** The Soot Particle Aerosol Mass Spectrometer (SP-AMS) instrument is a new technique that has been designed to detect and identify airborne refractory black carbon (rBC) particles using a low-power CW laser vaporizer with the intent of measuring the chemical

composition (refractory and nonrefractory) with minimal perturbations on the basic structure of the particles. The instrument is described in Onasch et al. (2012 and 2013) Publication 1a and b. SP-AMS mass spectra were measured for 10 types of rBC particles produced by industrial and combustion sources. The refractory carbon cluster ion distributions vary as a function of rBC particle type and serve as a finger print for the nature of the particles. The full rBC mass spectra vary as a function of production conditions (e.g. combustion fuel, flame, and fuel equivalence ratio (EQ)) and provides additional information about the source of the particles. We expect this technique to find application in the identification of the source and atmospheric history of airborne ambient rBC particles. As part of this work, we initiated a collaboration with Prof. Linsey Marr's research group at Virginia Tech to conduct measurements of single-component fullerene particles and fullerene mixtures, established using liquid chromatography, to investigate the potential for the SP-AMS to provide a quantitative measure of fullerenes in ambient particles. These studies are continuing. The instrument has already been used in several field studies. The SP-AMS has participated in the DOE ASR Biomass Burning Observation Project (BBOP) during the summer and fall of 2013 onboard the DOE G1 aircraft (Collier et al. in preparation), and in the 2010 CalNex field study. Continued development and application of the SP-AMS is part of our current DOE-funded project. The work on this project is described in Publications 1a, 1b, 1c, 1d.

**2. Optical Properties of Ambient rBC-Containing Particles.** Atmospheric rBC warms the Earth's climate, and its reduction has been targeted for near-term climate change mitigation. Models that include radiative forcing by BC assume internal mixing with non-BC aerosol components that can substantially enhance BC absorption, often by ~100%. The extent to which BC can theoretically be enhanced via lensing depends critically on the ratio  $R_{BC} = [NR-PM]/[BC]$  (the ratio of nonrefractory coating particulate matter to refractory black carbon). However, such model estimates have yet to be clearly validated through atmospheric observations. We used methods developed in our laboratory from previous DOE funded work to make direct *in situ* measurements of BC absorption enhancements ( $E_{abs}$ ) and mixing state for two California regions (Southern and Northern California) to address this issue during the CalNex 2010 campaign.

Specifically, we sampled ambient air sequentially through a bare tube and a thermal denuder using our SP-AMS and the UC Davis photoacoustic spectrometer. The ratio of these two measurements (denuded and non-denuded) provides a measure of the absorption enhancement caused by nonrefractory material coating the BC particles. The SP-AMS instrument explicitly measured the refractory black carbon mass concentration and the associated, chemically-resolved, nonrefractory mass on the rBC particles (i.e., coatings), providing a direct measure of  $R_{BC}$ . The measured  $R_{BC}$  was observed to increase with photochemical age, as expected due to secondary organic aerosol formation via photochemical oxidation and gas-to-particle condensation. However, the corresponding observed  $E_{abs}$  was small, ~6% on average at 532 nm, and increased weakly with photochemical age. The  $E_{abs}$  was less than predicted from observationally constrained theoretical calculations, suggesting that many climate models may overestimate warming by BC under some conditions. These ambient observations stand in contrast to our previous laboratory measurements that showed substantial  $E_{abs}$  for BC are possible (Cross et al., 2010; doi:10.1080/02786826.2010.482113). The field measurement results are described in Cappa et al. (2012a and 2013b).

To understand the observed low  $E_{abs}$  (<10%) for ambient BC-containing particles, we

collaborated with Prof. Chris Cappa from UC Davis (photoacoustic spectroscopy) and Prof. Jason Olfert (centrifugal particle mass analyzer; CPMA) from University of Alberta on a set of experiments with laboratory-generated soot particles, coated by dioctyl sebacate (DOS) or sulfuric acid. The absorption enhancement was measured for methane diffusion flame soot particles as a function of coating thickness. Preliminary analysis of the data appears to suggest a role for hydrophilic sulfuric acid and water vapor to produce particles with lower  $E_{\text{abs}}$  than hydrophobic DOS coated soot particles.

A three-week follow-up study was conducted in the spring of 2015. Sixteen people from seven research groups participated in the work. The data are currently being analyzed and seven manuscripts are in preparation. This project is described in detail as **Project 12** of this report.

As part of our current DOE-funded project, we will continue work to expand our understanding of the absorption enhancement process and how it is affected by single particle mixing state and morphological configurations. The work on this project is described in Publications 2a and 2b.

**3. Probing Refractory Black Carbon (rBC)-Containing Particle Configuration with a Single-Particle Soot Photometer (SP2).** A significant source of the uncertainty associated with refractory black carbon (rBC) radiative forcing is due to uncertainty in the chemical composition and morphology of the rBC-containing particle. While mass spectrometry is now routinely utilized to provide *in situ*, online analysis of particle composition, particle morphology analysis is still limited to off-line microscopy techniques. One class of instrumentation that may show promise towards addressing the lack of *in situ*, online particle morphology information is the Single Particle Soot photometer (SP2). Using the SP2 lagtime method, Sedlacek et al., (2012) interpreted the existence of a particle scattering signal after rBC incandescence as evidence of rBC inclusions being located at or near the surface of their non-refractory hosts. In an effort to further evaluate this initial interpretation, elucidate the origins of these signal conditions, and to explore the utility of this methodology for studying rBC-containing particle morphology, a series of experiments were carried out in our laboratories involving particle coagulation. This work suggests that the assumption of a core-shell configuration central to SP2-based mixing state analysis, must be used with caution. In light of this finding, it is recommended that SP2-based particle morphology mixing analysis should refrain from reporting coating thickness – as it invokes the assumption of a core-shell configuration – and rather report the ratio of non-refractory mass to rBC mass,  $R_{\text{BC}}$ , (where the non-refractory mass is standardized within the SP2 community to be sulfate). This work is ongoing in collaboration with Dr. A. Sedlacek III and is being continued in our currently funded DOE project. The work is described in Sedlacek et al. (2015), Publication 3.

**4. Relationship Between Chemical Composition and Optical Properties of SOA.** Brown carbon (BrC), which may include secondary organic aerosol (SOA), can be a significant climate-forcing agent via its optical absorption properties. However, the overall contribution of SOA to BrC remains poorly understood. In this project, in collaboration with Prof. Christopher Cappa's research group at UC-Davis, correlations between oxidation level and optical properties of SOA were examined. SOA was generated in a flow reactor in the absence of  $\text{NO}_x$  by OH oxidation of gas-phase precursors used as surrogates for anthropogenic (naphthalene, tricyclo-[5.2.1.0<sup>2,6</sup>]decane [JP-10]), biomass burning (guaiacol), and biogenic ( $\alpha$ -pinene) emissions. SOA chemical composition was characterized with a time-of-flight aerosol mass spectrometer. The mass spectra yielded oxygen-to-carbon (O/C) ratios, used as a measurable surrogate for SOA

oxidation level that ranged from 0.29 to 1.29. SOA mass-specific absorption cross sections (MAC) and refractive indices were calculated from real-time photoacoustic spectrometry (PAS) measurements at 405 and 532 nm and from UV-Vis spectrometry measurements of methanol extracts of filter-collected particles (300 to 600 nm). At 405 nm, SOA MAC values and imaginary refractive indices ranged from  $<0.001$  to  $0.088 \text{ m}^2 \text{ g}^{-1}$  and  $1.9 \times 10^{-4}$  to  $3.6 \times 10^{-3}$ , respectively, increasing with SOA oxidation level. SOA light absorption decreased with increasing wavelength, leading to negligible absorption at 532 nm. Real refractive indices ( $n$ ) of SOA at 405 nm ranged from 1.45 to 1.66 and for a given precursor changed at a rate of  $\Delta(n)/\Delta(\text{O/C}) = -0.055$  to  $-0.11$ . Comparison with literature studies suggests that under typical polluted conditions the effect of  $\text{NO}_x$  on SOA absorption is small. SOA may contribute significantly to atmospheric BrC, with the magnitude dependent on both precursor and oxidation level. This work is continuing and is being expanded under our current DOE-Funded project. Part of the work is described in Lambe et al. (2013) Publication 4.

**5. The Deposition Ice Nucleation and Immersion Freezing Potential of Amorphous SOA: Pathways For Ice and Mixed-Phase Cloud Formation.** Secondary organic aerosol (SOA) generated from the oxidation of organic gases are ubiquitous in the atmosphere, but their interaction with water vapor and their ice cloud formation potential at low temperatures remain highly uncertain. In collaboration with Prof. Daniel Knopf's research group at Stony Brook University, measured onset conditions of water uptake and ice nucleation by amorphous SOA particles generated from the oxidation of naphthalene with OH radicals. Water uptake above 230 K was governed by the oxidation level of the SOA particles expressed as oxygen-to-carbon (O/C) ratio, followed by moisture-induced phase transitions and immersion freezing. For temperatures in the range 200 to 230 K, SOA particles nucleated ice via deposition mode from supersaturated water vapor independent of O/C ratio at relative humidity with respect to ice ( $\text{RH}_{\text{ice}}$ )  $\sim 10$ – $15\%$  below homogeneous ice nucleation limits. The glass transition temperature ( $T_g$ ) for the amorphous SOA particles was derived as a function of two parameters: (1) relative humidity (RH) with respect to water and (2) oxidation level of the SOA. The data show that particle phase and viscosity govern the particle response to temperature and RH and provide a straightforward interpretation for the observed different heterogeneous ice nucleation pathways and water uptake by the laboratory-generated SOA and field-collected particles. Since SOA particles undergo glass transitions, these observations suggest that atmospheric SOA are potentially important for ice cloud formation and climate. To assess whether SOA may exhibit atmospherically relevant influence on IN activity, we will continue our collaboration with Dr. Knopf to study IN activities of SOA over a wide range of relevant precursors and oxidation states. The work is described in Wang et al. (2012) Publication 5.

**6. Phase and Phase Transition Studies of SOA.** The physical phase (solid or liquid) of SOA particles has important implications for a number of atmospheric processes. In collaboration with colleagues from Finland, we investigated the phase of SOA particles produced in the PAM reactor by OH oxidation of various anthropogenic and biogenic SOA precursors. The phase was determined by measuring particle bounce behavior after inertial impaction on a polished steel substrate. The main findings of the study are: (1) Biogenic and anthropogenic SOA particles are typically solid or semi-solid until relative humidity rises above 55%; (2) Long-chain alkanes produce liquid SOA particles at low oxidation levels that solidify with increasing oxidation levels; (3) Mixing sulfuric acid with the SOA reduces the threshold of humidity-induced phase changes; and (4) An increase in the molecular mass of the SOA precursor increases the threshold

of humidity-induced phase changes. A continuation of this work is planned in collaboration with Prof. Annele Virtanen as part of the currently funded DOE studies. This work is described in Saukko et al. (2012) Publication 6.

**7. Characterization of Aerosol Photooxidation Flow Reactors: Heterogeneous Oxidation, Secondary Organic Aerosol Formation and Cloud Condensation Nuclei Activity Measurements.** We studied the performance of the Toronto Photo-Oxidation Tube (TPOT) and Potential Aerosol Mass (PAM) flow tube reactors under a variety of experimental conditions. The PAM system was designed with lower surface-area-to-volume (SA/V) ratio to minimize wall effects; the TPOT reactor was designed to study heterogeneous aerosol chemistry where wall loss can be independently measured. The following studies were performed: (1) transmission efficiency measurements for CO<sub>2</sub>, SO<sub>2</sub>, and DOS particles, (2) H<sub>2</sub>SO<sub>4</sub> yield measurements from the oxidation of SO<sub>2</sub>, (3) residence time distribution (RTD) measurements for CO<sub>2</sub>, SO<sub>2</sub>, and BES particles, (4) aerosol mass spectra, O/C and H/C ratios, and cloud condensation nuclei (CCN) activity measurements of BES particles exposed to OH radicals, and (5) aerosol mass spectra, O/C and H/C ratios, CCN activity, and yield measurements of secondary organic aerosol (SOA) generated from gas-phase OH oxidation of m-xylene and  $\alpha$ -pinene. OH exposures ranged from  $(2.0 \pm 1.0) \times 10^{10}$  to  $(1.8 \pm 0.3) \times 10^{12}$  molec cm<sup>-3</sup> s. Where applicable, data from the flow tube reactors were compared with published results from the Caltech smog chamber. The TPOT yielded narrower RTDs. However, its transmission efficiency for SO<sub>2</sub> was lower than that for the PAM. Transmission efficiency for BES and H<sub>2</sub>SO<sub>4</sub> particles was size-dependent and was similar for the two flow tube designs. Oxidized BES particles had similar O/C and H/C ratios and CCN activity at OH exposures greater than  $10^{11}$  molec cm<sup>-3</sup> s, but different CCN activity at lower OH exposures. The O/C ratio, H/C ratio, and yield of m-xylene and  $\alpha$ -pinene SOA were strongly affected by reactor design and operating conditions, with wall interactions having the strongest influence on SOA yield. At comparable OH exposures, flow tube SOA was more oxidized than smog chamber SOA, possibly because of faster gas-phase oxidation relative to particle nucleation. SOA yields were lower in the TPOT than in the PAM, but CCN activity of flow-tube-generated SOA particles was similar. For comparable OH exposures,  $\alpha$ -pinene SOA yields were similar in the PAM and Caltech chambers, but m-xylene SOA yields were much lower in the PAM compared to the Caltech chamber. Further, studies comparing SOA produced in flow reactors, smog chambers and the ambient are in progress. The work was published Lambe et al. 2011, Publication 7

**8. Relationship Between Aerosol Oxidation Level and Hygroscopic Properties of SOA.** Laboratory experiments investigated the relationship between oxidation level and hygroscopic properties of secondary organic aerosol (SOA) particles generated via OH radical oxidation in an aerosol flow reactor. The hygroscopic growth factor at 90% RH (HGF<sub>90%</sub>), the CCN activity ( $\kappa_{\text{ORG,CCN}}$ ) and the level of oxidation (atomic O:C ratio) of the SOA particles were measured. Both HGF<sub>90%</sub> and  $\kappa_{\text{ORG,CCN}}$  increased with O:C; the HGF<sub>90%</sub> varied linearly with O:C, while  $\kappa_{\text{ORG,CCN}}$  mostly followed a nonlinear trend. An average HGF<sub>90%</sub> of 1.25 and  $\kappa_{\text{ORG,CCN}}$  of 0.19 were measured for O:C of 0.65, in agreement with results reported for ambient data. The  $\kappa_{\text{ORG}}$  values estimated from the HGF<sub>90%</sub> ( $\kappa_{\text{ORG,CCN}}$ ) were 20 to 50% lower than measured  $\kappa_{\text{ORG,CCN}}$  values for all SOA particles except 1,3,5-trimethylbenzene (TMB), the least hygroscopic of the SOA systems. Within the limitations of instrumental capabilities, we show that differences in

hygroscopic behavior among the investigated SOA systems may correspond to differences in elemental composition. This work is described in Massoli et al. (2010) and Pajunoja et al (2015), Publications 8a and 8b.

**9. Studies of Chemical Composition, Hygroscopicity, and CCN Activity of SOA and Oxidized Primary Organic Aerosol (OPOA).** Laboratory SOA and OPOA were produced from the oxidation of fourteen precursors representing atmospherically relevant biogenic and anthropogenic sources. The SOA and OPOA particles were generated via controlled exposure of precursors to OH radicals and/or O<sub>3</sub> in a PAM flow reactor. Cloud condensation nuclei (CCN) activity of SOA and OPOA was measured as a function of OH exposure and characterized as a function of O/C ratio, which was used as a surrogate for the oxidation level. CCN activity, characterized by the hygroscopicity parameter  $\kappa_{org}$ , ranged from  $8.4 \times 10^{-4}$  to 0.28 over measured O/C ratios ranging from 0.05 to 1.42. This range of  $\kappa_{org}$  and O/C ratio is significantly wider than has been previously obtained (Jimenez et al. 2009; Chang et al. 2010), and extends our previous work (Massoli et al. 2010). To first order, the  $\kappa_{org}$ -to-O/C relationship is represented by a linear function of the form  $\kappa_{org} = (0.18 \pm 0.04) \times O/C + 0.03$ , suggesting that a simple, semi-empirical parameterization of OOA hygroscopicity and oxidation level can be defined for use in chemistry and climate models. We continue to explore the connection between the chemistry, phase, and mixing state of carbonaceous particles during the during the currently funded DOE project. The work is described in Lambe et al. (2011b) Publication 9a and 9b.

**10. Functionalization and Fragmentation Reactions of Alkane SOA and Comparisons with Chamber and Ambient SOA.** Recent field measurements suggest that alkanes may be important precursors to SOA formation, particularly those alkanes with carbon numbers ranging from approximately 14 to 18 that exist in the gas phase but are difficult to measure with established techniques. In this work, functionalization and fragmentation reaction pathways were determined for SOA generated from the OH oxidation of alkane precursors in the absence of NO<sub>x</sub>. Secondary organic aerosol (SOA) was produced from the OH oxidation of *n*-decane (*n*-C<sub>10</sub>), *n*-pentadecane (*n*-C<sub>15</sub>), *n*-heptadecane (*n*-C<sub>17</sub>), tricyclo[5.2.1.0<sup>2,6</sup>]decane and from vapors of Southern Louisiana crude oil and diesel fuel. In the range of OH exposures studied, the SOA yield first increases and then decreases, showing the transition from functionalization to fragmentation processes. Multiple gas-phase oxidation reactions produce SOA with predominately carboxylic acid functional groups, concurrent with significant fragmentation of carbon-carbon bonds. Van Krevelen diagrams showing H/C ratio as a function of O/C ratio may identify contributions of alkane precursors to ambient SOA. The crude oil SOA mass spectra generated by the PAM, the MIT environmental chamber, and in the ambient atmosphere of the Gulf are highly correlated. The work is described in Lambe et al. (2012, Publication 9b) and Bahreini et al. (2012). Publication 10

**11. Modeling the Evolution of  $\alpha$ -Pinene SOA Volatility and Oxidation Level Using the Two-Dimensional Volatility Basis Set (2D-VBS) Approach.** A model has been developed to simulate the formation and evolution of secondary organic aerosol (SOA) and was compared to data produced in a Potential Aerosol Mass (PAM) flow reactor and a large environmental chamber. The model framework is based on the two-dimensional volatility basis set approach (2D-VBS), in which SOA oxidation products in the model are distributed on the 2D space of effective saturation concentration ( $C_i^*$ ) and oxygen-to-carbon ratio (O:C). The modeled organic aerosol mass concentrations ( $C_{OA}$ ) and O:C agree with laboratory measurements within

estimated uncertainties. However, while both measured and modeled O:C increase with increasing OH exposure as expected, the increase of modeled O:C is rapid at low OH exposure and then slows as OH exposure increases while the increase of measured O:C is initially slow and then accelerates as OH exposure increases. A global sensitivity analysis indicates that modeled  $C_{OA}$  values are most sensitive to the assumed values for the number of  $C_i^*$  bins, the heterogeneous OH reaction rate coefficient, and the yield of first-generation products. Modeled SOA O:C values are most sensitive to the assumed O:C of first-generation oxidation products, the number of  $C_i^*$  bins, the heterogeneous OH reaction rate coefficient, and the number of O:C bins. All these sensitivities vary as a function of OH exposure. The sensitivity analysis indicates that the 2D-VBS model framework may require modifications to resolve discrepancies between modeled and measured O:C as a function of OH exposure. The work is described in Chen et al. (2013), Publication 11.

**12. Collaborative Study no. 4 of Black Carbon containing aerosol particles (BC4): Instrumentation and Optical properties, March 23 to April 10, 2015.** Atmospheric black carbon (BC), mostly in the form of soot particles, absorbs light and produces local heating of the atmosphere and may lead to warming of the Earth's climate. Models that include radiative forcing by BC assume internal mixing with non-BC aerosol components that can substantially enhance BC absorption, often by ~100%. The extent to which absorption by BC can theoretically be enhanced via lensing depends critically on the ratio of non-refractory coating particulate matter to refractory black carbon as well as on the morphology of the coated particles and the chemical composition of the coating material. However, such model estimates have yet to be clearly validated by atmospheric or laboratory measurements.

**The goals of the project were twofold:**

**A.** *To inter-compare and calibrate new and redesigned instruments for the measurement of optical properties of black carbon-containing soot particles.* This was done with laboratory generated nascent and oxidized soot as a function of particle mass. The optical properties of nascent and oxidized soot were characterized more accurately than was possible in previous studies. The greater accuracy of characterization was due to improved techniques for generation of monodisperse particle size/mass sampling. Soot was oxidized by exposure to OH equivalent to 0-3 days of atmospheric lifetime. The optical properties were measured over a range of wavelengths from 301 nm to 687 nm, spanning in a single set of studies a wider range of atmospherically relevant optical wavelengths than has been to date possible.

**B.** *To characterize the optical properties of soot coated with SOA and/or  $H_2SO_4$ .* Here of specific interest is the absorption enhancement produced by the non-absorbing coatings. In most laboratory studies (but not all), non-absorbing coatings are observed to increase light absorption by BC containing particles. However, in field experiments absorption enhancement is observed in some studies but not in others. Enhancement data on well-characterized cores with well-defined coatings are still lacking. The purpose of this study was to provide such data.

The coatings were generated by oxidizing gas phase precursors  $\alpha$ -pinene, naphthalene and  $SO_2$ . These compounds were selected as surrogates respectively for biogenic and anthropogenic gas phase species emitted into the atmosphere.  $SO_2$  when oxidized by OH yields sulfuric acid that is a ubiquitous component of the atmosphere. Coatings were deposited on the well-characterized soot particles and optical properties were measured as a function of SOA coating thickness and optical wavelength. Many days of ambient particle sampling was also done with ambient aerosol extracted from the adjacent Beacon Street.

**Following is a list of participants and the instrumentation they brought to the study:**

**BC/ARI group:** Lindsay Wolff, Andy Lambe, Yatish Parmar, James Brogan, Tim Onasch, Andy Freedman, Leah Williams and Paul Davidovits. Instrumentation: Production and processing and coating of particles: Vertical, stable inverted soot flame source, a PAM reactor providing controlled oxidative aging of such particles via OH and O<sub>3</sub> reactions over equivalent atmospheric lifetimes ranging from hours to multiple days. Instruments for measuring and controlling particle size composition and mass distributions: SMPS (mobility diameter), AMS (non refractory composition and aerodynamic diameter), Centrifugal Particle Mass Analyzer (CPMA, particle mass), SP-AMS (non-refractory and refractory composition and aerodynamic diameter).

**Chris Cappa group, UC Davis:** Chris Cappa, Taylor Helgestad. Instrumentation: Photoacoustic Spectrometer (PAS)/ Cavity Ring-down (CRD) instrument capable of simultaneously measuring light absorption and extinction at two distinct wavelengths (405 and 532 nm). This instrument provides concurrent and very sensitive measures of light absorption (PAS) and light extinction due to scattering and absorption (CRD).

**Jesse Kroll group, MIT:** Ellie Browne, Gabriel Isaacman-Wertz. Instrumentation: A single scattering albedo (SSA) monitor operating at 630 nm was provided by MIT/ARI. The instrument is capable of measuring the extinction and scattering of light at a single wavelength. From this information, the particle absorption may be calculated. CPMA for particle mass selection.

**Geoffrey Smith group, U Georgia Athens:** Geoff Smith, Al Fischer. Instrumentation: UV-VIS photoacoustic spectrometer, capable of measuring gas phase and aerosol absorption at 8 distinct wavelengths ranging from 301 to 678 nm also a two broad-band cavity-enhanced extinction monitors that operates over 30 nm band widths in the UV (360-390 nm) and red (660-690 nm) regions of the electromagnetic spectrum.

**Claudio Mazzoleni group, Michigan Technical University:** Swarup China. Instrumentation: Collection of particles on grids for analysis via Scanning Electron Microscope (SEM) and Tunneling Electron Microscope (TEM). This data will be used to determine particle morphology.

**Brookhaven National Lab:** Art Sedlacek. Instrumentation: An SP2 instrument owned by DOE compares time evolution of the scattered and incandescent light. Such data can be interpreted in terms the position of the black carbon core and the SOA material. That is, whether the SOA coating surrounds the core or whether the coating material is separated from the core.

**Preliminary Results; a brief summary.**

Preliminary analysis of the data indicates that the various instruments designed to measure the same parameters agree with each other to better than 20%. Specifically, the mass absorption coefficients (MACs) determined with the UV-Vis PAS system were, on average, within ~15%, 20% of the MACs measured with the CRD-PAS system at 405, 532 nm and <10% from the 632 nm MACs determined with the CAPS-SSA monitor results.

In the experiments performed with nascent soot, the MAC values are independent of particle mass, as expected. The data collected in this study were more accurate than any study we, and perhaps many other groups, have ever collected in the past. Improvements over previous experiments involve size as well as mass selecting the soot in order to ensure that particles entering optical instruments are monodisperse in mass and don't include larger, multiply charged particles that may not be detectable with SMPS but may greatly affect the optical measurements.

In previous studies, in order to avoid multiply charged particles, the dilution flow on the



fuel was changed, which we have found affects the composition of the soot and thus its optical properties. By size and mass selecting, we can study the optical properties across an order of magnitude in mass without changing the flame conditions.

In these experiments performed with well-defined coatings, all non-absorbing coatings produced absorption enhancement when the mass ratio of coating-to-core was greater than  $\sim 1:1$ . The enhancement produced by sulfuric acid and  $\alpha$ -pinene SOA coatings are about the same and are, to a first approximation, what would be expected from Mie-theory for a coat-core structure. Naphthalene SOA leads to slightly lower enhancements, which do not seem to be explained by differences in the refractive index of the SOA, perhaps suggesting a different morphology than the other coatings. SP2 and TEM/SEM images will be used to further interpret the absorption enhancement results.

These results together with earlier SP2 studies suggest that in studies where measured SOA materials do not produce enhancement or that the enhancement is lower than expected by Mie theory, the SOA observed together with the BC particle does not coat the soot core but is likely separated from it either by phase separation or by coalescence.

Ambient data collected from Beacon Street, a busy artery between Boston and the surrounding suburbs, is still under analysis. However, preliminary data suggests that a substantial fraction of the particles sampled were mixtures of refractory and non-refractory materials. Whether absorption enhancement was observed is still under investigation.

A full analysis of the data is in progress and when completed, the results will be submitted for publication in formats readily usable in climate models. We anticipate that eight manuscripts will describe the full range of results obtained in the BC4 studies.

## **BC4 MANUSCRIPTS IN PREPARATION AND PLANNED**

### **1. Nascent soot manuscripts.**

1.1. Nascent soot optical properties. We have the ability to size and mass select soot particles without having to change the flame conditions. We were able to size and mass select while keeping the multiply charged particles to a negligible minimum. The data obtained in these optical studies suggest that the absorption coefficients are mass independent and the Single Scattering Albedo (SSA) increases linearly of the with mass across the range of masses from 0.8-8 fg. Tim Onasch of the BC/ARI group is leading the manuscript preparation.

1.2. Oxidized soot chemical and optical properties. By combining SP-AMS, TEM/SEM and CPMA data we can track chemical and optical property changes of flame soot as a function of oxidation. MAC increases upon denuding, while organic signal goes down. By contrast, the optical properties and organic mass of un-oxidized denuded soot do not change. BC/ARI and/or MIT. Combined optical measurements (MAC, AAE, etc), chemical composition, most specifically H-to-C (SP-AMS), graphitization/ morphology (TEM) all provide proxies for soot maturity. In this manuscript we will map out the maturity of soot on an axis similar to Bond and Bergstrom (2006) showing how "maturity" affects the optical properties of rBC. These experimental results may be combined with theoretical calculations (Tmatrix, Mie, RDG, DDA). Lindsay Wolff of the BC/ARI group is leading the manuscript preparation.

### **2. Coated soot manuscripts**

2.1. Mie closure manuscript. The manuscript will compare results obtained with soot particles coated with aP SOA, naphthalene SOA and H<sub>2</sub>SO<sub>4</sub> to Mie Theory predictions to determine how

well Eabs is predicted by Mie theory. We will use complex refractive indices from methane diffusion flame bare soot data. Implications for modeling aerosol direct climate effects with Mie theory will be evaluated. Lindsay Wolff of the BC/ARI group is leading the manuscript preparation.

2.2. Coating comparison paper. In this manuscript we will explore the degree to which morphology affects absorption enhancement. We will use TEM/SEM as well as the SP2 data to get morphological information about the coatings. We will also examine chemical composition of coatings affects the observed Eabs. Lindsay Wolff of the BC/ARI group is leading the manuscript preparation.

### 3. Overview Manuscripts

3.1. Instrument intercomparison manuscript. Comparison of optical instruments for the study of nascent, oxidized and coated soot (absorption, extinction, scattering). Comparison of SP-AMS and CPMA for total mass determination and also compare to SP2 to SP-AMS for nascent experiments and SP-AMS to SP2 and CPMA for determination of mass of black carbon core. University of Georgia group is leading the manuscript preparation.

3.2. Particle chemistry/mass measurements. Data are being analyzed to yield comparison of SP-AMS to per particle mass determination by CPMA for various types of particles (nascent, oxidized, coated, coated+denuded). What can we learn about the particle chemistry (and/or our ability to detect) based on these comparisons? How do the SP-AMS and SP2 compare for different particle chemistries (nascent, oxidized, coated, coated+denuded). Can we learn anything new about the particle morphology? Manuscript lead groups: MIT//BNL/BC

### ONGOING STUDIES.

As indicated in the report DOE-funded studies are continuing on projects central to understanding the role of aerosol, particularly carbonaceous aerosol in climate forcing. Among the projects planned are: (1) characterization of phase, hygroscopicity, and ice nuclei (IN)-forming potential (2) characterization of single-particle mixing state, and (3) characterization of optical properties of rBC particles mixed with inorganics, SOA, and biomass burning organic aerosols (BBOA). These studies are related to several current and planned ARM-funded studies.

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**Publication 1a:** Onasch, T. B., Trimborn, A. M., Fortner, E. C., Jayne, J. T., Kok, G. L., Williams, L. R., Davidovits, P., et al. (2012). Soot Particle Aerosol Mass Spectrometer: Development, Validation, and Initial Application. *Aerosol Science and Technology*, 46(7), 804–817. doi:10.1080/02786826.2012.663948

**Publication 1b:** Onasch, T. B., Fortner, E. C., Trimborn, A. M., Lambe, A. T., Tiwari, A.J. Marr, L.C., Coebin, J.C., Mensa, A.A., Williams, L.R., Davidovits, P. Worsnop, D. R. (2013b). Investigation of SP-AMS Carbon Ion Distributions as a Function of Black Carbon Particle Type. *Aerosol Science and Technology*, 49, 409-422, 2015. Doi: 10.1080/02786826.2015.1039959

**Publication 1c:** Massoli, P., Cappa C.D., Hayden, K., Canagaratna, M.R., Nuamaan, I., Li,

S.M., Sueper, D.T., Bates, T.S., Quinn, P.K., Worsnop, D.R., and Onasch, T.B. (2013): Characterization of black carbon-containing particles from soot particle aerosol mass spectrometer (SP-AMS) measurements on the *R/V Atlantis* during CalNex 2010, in preparation.

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**Publication 2b:** Cappa, C. D., Onasch, T. B., Massoli, P., Worsnop, D. R., Bates, T. S., Cross, E. S., Davidovits, P., Hakala, J., Hayden, K. L., Jobson, B. T., Kolesar, K. R., Lack, D. A., Lerner, B. M., Li, S.-M., Mellon, D., Nuaaman, I., Olfert, J. S., Petaja, T., Quinn, P. K., Song, C., Subramanian, R., Williams, E. J. and Zaveri, R. A.: Response to Comment on “Radiative Absorption Enhancements Due to the Mixing State of Atmospheric Black Carbon,” *Science* (80-. ), 339(6118), 393–393, doi:10.1126/science.1230260, 2013.

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**Publication 4:** Lambe, A. T., Cappa, C. D., Massoli, P., Onasch, T. B., Forestieri, S. D., Martin, A. T., Cummings, M. J., Croasdale, D. R., Brune, W. H., Worsnop, D. R., and Davidovits, P. (2013). Relationship between oxidation level and optical properties of secondary organic aerosol. *Environ. Sci. Technol.*, 2013, 47, 6349-6357.

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**Publication 6:** Saukko, E., Lambe, A. T., Massoli, P., Koop, T., Wright, J. P., Croasdale, D. R., Pedernera, D. A., Onasch, T. B., Laaksonen, A., Davidovits, P., Worsnop, D. R. and Virtanen, A. (2012b): Humidity-dependent phase state of SOA particles from biogenic and anthropogenic precursors, *Atmos. Chem. Phys.*, 12(16), 7517–7529, doi:10.5194/acp-12-7517-2012.

**Publication 7:** Lambe, A. T., Ahern, A. T., Williams, L. R., Slowik, J. G., Wong, J. P. S., Abbatt, J. P. D., Brune, W. H., Ng, N.L., Wright, J.P., Croasdale, D.R., Worsnop, D.R., Davidovits, P., Onasch, T.B. (2011a). Characterization of aerosol photooxidation flow reactors: heterogeneous oxidation, secondary organic aerosol formation and cloud

condensation nuclei activity measurements. *Atmospheric Measurement Techniques*, 4(3), 445–461. doi:10.5194/amt-4-445-2011

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**Publication 8b:** Aki Pajunoja, Aki, Andrew T. Lambe, Jani Hakala, Narges Rastak, Molly J. Cummings, James F. Brogan, Liqing Hao, Mikhail Paramonov, Juan Hong, Nønne L. Prisle, Jussi Malila, Sami Romakkaniemi, Kari E. J. Lehtinen, Ari Laaksonen, Markku Kulmala, Paola Massoli, Timothy B. Onasch, Neil M. Donahue, Ilona Riipinen, Paul Davidovits, Douglas R. Worsnop, Tuukka Petäjä, and Annele Virtanen, Adsorptive uptake of water by semisolid secondary organic aerosols, 2015, *Geophys. Res. Lett.*, 42, doi:10.1002/2015GL063142.

**Publication 9a:** Lambe, A. T., Onasch, T. B., Massoli, P., Croasdale, D. R., Wright, J. P., Ahern, a. T., Williams, L. R., et al. (2011b). Laboratory studies of the chemical composition and cloud condensation nuclei (CCN) activity of secondary organic aerosol (SOA) and oxidized primary organic aerosol (OPOA). *Atmospheric Chemistry and Physics*, 11(17), 8913–8928. doi:10.5194/acp-11-8913-2011

**Publication 9b:** Lambe, A. T., Onasch, T. B., Croasdale, D. R., Wright, J. P., Martin, A. T., Franklin, J. P., Massoli, P., et al. (2012). Transitions from Functionalization to Fragmentation Reactions of Laboratory Secondary Organic Aerosol (SOA) Generated from the OH Oxidation of Alkane Precursors. *Environmental Science & Technology*, 46(10), 5430–5437. doi:10.1021/es300274t

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**Publication 11:** Chen, S., Brune, W. H., Lambe, A. T., Davidovits, P., & Onasch, T. B. (2013). Modeling organic aerosol from the oxidation of  $\alpha$ -pinene in a Potential Aerosol Mass (PAM) chamber. *Atmospheric Chemistry and Physics*, 13(9), 5017–5031. doi:10.5194/acp-13-5017-2013

### **Undergraduate Student Researchers.**

During the past four years the following eight undergraduate students have worked in our research group: Adam Ahern, Alexander Martin, David Croasdale, Justin Wright, Molly Cummings, James Brogan, Yatish Parmar, Taehyun Lee.

The students involved in our research projects worked at least 12 hours a week during the academic year and full time during summer. They learned advanced experimental techniques including laser and mass and optical spectroscopic techniques and methods of data analysis. They also learned the use of advanced computer programs as experimental and analytical tools. The students regularly presented their experimental results at group seminars. Each of these students are co-authors on at least one refereed publication.

The three students James Brogan Yatish Parmar Taehyun Lee are currently working in the laboratory. The other students are at various stages of their graduate work.

### **Post-doctoral Fellows.**

Andrew Lambe, Lindsay Renbaum-Wolff.

### **Glossary of Terms**

AAE	Absorption Ångstrom Exponent
AMS	Aerosol Mass Spectrometer
BBOP	Biomass Burning Observation Project
BC	Black Carbon
BrC	Brown Carbon
CAPS	Cavity Attenuated Phase-Shift Spectroscopy
CCN	Cloud Condensation Nucleus
CPMA	Centrifugal Particle Mass Analyzer
CRD	Cavity Ring-Down
DDA	Discrete dipole approximation
$E_{abs}$	absorption enhancements
EQ	Equivalence Ratio
HGF	Hygroscopic Growth Factor
IN	Ice Nucleation
MAC	Mass Specific Absorption Cross section
NR-PM <sub>BC</sub>	Non-refractory particulate matter
OPOA	Oxidized Primary Organic Aerosol
PAM	Potential Aerosol Mass flow tube reactor
PAS	Photoacoustic Spectrometer
rBC	Refractory Black Carbon
RDG	Rayleigh-Debye-Gans
RH	Relative Humidity
SEM	Scanning Electron Microscope
SMPS	Scanning Mobility Particle Sizer
SOA	Secondary Organic Aerosol
SP-AMS	Single Particle AMS
SP2	Single Particle Soot Photometer
SSA	Single Scattering Albedo
TEM	Tunneling Electron Microscope
TPOT	Toronto Photo-Oxidation Tube